

IN THE CLAIMS

1-7. (Cancelled)

8. (Previously Presented) A method for depositing a copper-containing seed layer onto a barrier layer, comprising:

providing a substrate comprising the barrier layer disposed on a substrate surface, wherein the barrier layer has a barrier surface selected from the group consisting of a tungsten surface, a tungsten nitride surface, a titanium surface, a titanium nitride surface, a cobalt surface, a ruthenium surface, a nickel surface, and a silver surface;

exposing the substrate to a first copper solution comprising complexed copper ions and having a pH value of less than 7, wherein the complexed copper ions are derived from a copper source selected from the group consisting of copper citrate, copper borate, copper tartrate, copper oxalate, derivatives thereof, and combinations thereof;

applying a first electrical bias across the substrate surface to chemically reduce the complexed copper ions to deposit a copper seed layer onto the barrier surface; and

depositing a copper gap-fill layer by:

exposing the substrate to a second copper solution comprising free-copper ions; and

applying a second electrical bias across the substrate surface to deposit the copper gap-fill layer onto the copper seed layer.

9. (Previously Presented) The method of claim 8, further comprising depositing a copper bulk-fill layer by:

exposing the substrate to a third copper solution comprising free-copper ions; and

applying a third electrical bias across the substrate surface to deposit the copper bulk-fill layer onto the copper gap-fill layer.

10. (Original) The method of claim 9, wherein at least one leveling agent is added to the second copper solution to form the third copper solution.

11-19. (Cancelled)

20. (Previously Presented) A method for depositing a copper-containing seed layer onto a barrier layer, comprising:

providing a substrate comprising the barrier layer disposed on a substrate surface, wherein the barrier layer has a barrier surface selected from the group consisting of a tungsten surface, a tungsten nitride surface, a titanium surface, a titanium nitride surface, a cobalt surface, a ruthenium surface, a nickel surface, and a silver surface;

exposing the substrate to a complexed copper solution comprising complexed copper ions reducing the complexed copper ions with a first electrical bias to form a copper seed layer on the barrier surface; and

depositing a copper gap-fill layer by:

exposing the substrate to a first copper solution comprising free-copper ions; and

applying a second electrical bias across the substrate surface to deposit the copper gap-fill layer onto the copper seed layer.

21. (Previously Presented) The method of claim 20, further comprising depositing a copper bulk-fill layer by:

exposing the substrate to a second copper solution comprising free-copper ions; and

applying a third electrical bias across the substrate surface to deposit the copper bulk-fill layer onto the copper gap-fill layer.

22. (Previously Presented) The method of claim 21, wherein at least one leveling agent is added to the first copper solution to form the second copper solution.

23-30. (Cancelled)

31. (Previously Presented) A method for depositing a copper-containing seed layer onto a barrier layer, comprising:

providing a substrate comprising the barrier layer disposed on a substrate surface, wherein the barrier layer has a barrier surface selected from the group consisting of a tungsten surface, a tungsten nitride surface, a titanium surface, a titanium nitride surface, a cobalt surface, a ruthenium surface, a nickel surface, and a silver surface;

exposing the substrate to a complexed copper solution comprising complexed copper ions derived from a copper source selected from the group consisting of copper citrate, copper borate, copper tartrate, copper oxalate, derivatives thereof, and combinations thereof;

reducing the complexed copper ions with a first electrical bias to form a copper seed layer on the barrier surface, wherein the first electrical bias has a current density of less than about 10 mA/cm² across the substrate surface; and

depositing a copper gap-fill layer by:

exposing the substrate to a second copper solution comprising free-copper ions; and

applying a second electrical bias across the substrate surface to deposit the copper gap-fill layer onto the copper seed layer.

32. (Previously Presented) The method of claim 31, further comprising depositing a copper bulk-fill layer by:

exposing the substrate to a third copper solution comprising free-copper ions; and

applying a third bias across the substrate surface to deposit the copper bulk-fill layer onto the copper gap-fill layer.

33. (Original) The method of claim 32, wherein at least one leveling agent is added to the second copper solution to form the third copper solution.

34-36. (Cancelled)

37. (Previously Presented) The method of claim 8, wherein the copper seed layer is deposited on the entire barrier surface.

38. (Previously Presented) The method of claim 8, wherein the copper source is copper citrate.

39. (Previously Presented) The method of claim 38, wherein the first copper solution contains a copper concentration within a range from about 0.02 M to about 0.8 M.

40. (Previously Presented) The method of claim 39, wherein the first electrical bias generates a current density of less than about 10 mA/cm² across the substrate surface.

41. (Previously Presented) The method of claim 39, wherein the first electrical bias generates a current density within a range from about 0.5 mA/cm² to about 3 mA/cm² across the substrate surface.

42. (Previously Presented) The method of claim 38, wherein the copper seed layer has a thickness of less than about 200 Å.

43. (Previously Presented) The method of claim 38, wherein the pH value is within a range from about 4.5 to about 6.5.

44. (Previously Presented) The method of claim 8, wherein the barrier layer consists essentially of cobalt, ruthenium, nickel, or tungsten.

45. (Previously Presented) The method of claim 20, wherein the copper seed layer is deposited on the entire barrier surface.

46. (Previously Presented) The method of claim 20, wherein the complexed copper ions are derived from a copper source selected from the group consisting of copper citrate, copper borate, copper tartrate, copper oxalate, derivatives thereof, and combinations thereof.
47. (Previously Presented) The method of claim 20, wherein the complexed copper solution comprises copper citrate.
48. (Previously Presented) The method of claim 47, wherein the complexed copper solution contains a copper concentration within a range from about 0.02 M to about 0.8 M.
49. (Previously Presented) The method of claim 48, wherein the first electrical bias generates a current density of less than about 10 mA/cm^2 across the substrate surface.
50. (Previously Presented) The method of claim 48, wherein the first electrical bias generates a current density within a range from about 0.5 mA/cm^2 to about 3 mA/cm^2 across the substrate surface.
51. (Previously Presented) The method of claim 47, wherein the copper seed layer has a thickness of less than about 200 Å.
52. (Previously Presented) The method of claim 47, wherein the complexed copper solution comprises a pH value within a range from about 4.5 to about 6.5.
53. (Previously Presented) The method of claim 31, wherein the copper seed layer is deposited on the entire barrier surface.
54. (Previously Presented) The method of claim 31, wherein the complexed copper solution comprises copper citrate.

55. (Previously Presented) The method of claim 54, wherein the complexed copper solution contains a copper concentration within a range from about 0.02 M to about 0.8 M.

56. (Previously Presented) The method of claim 55, wherein the current density is within a range from about 0.5 mA/cm² to about 3 mA/cm² across the substrate surface.

57. (Previously Presented) The method of claim 54, wherein the copper seed layer has a thickness of less than about 200 Å.

58. (Previously Presented) The method of claim 54, wherein the complexed copper solution has a pH value within a range from about 4.5 to about 6.5.

59. (Previously Presented) A method for depositing a copper-containing seed layer onto a barrier material layer, comprising:

- providing a substrate having a ruthenium barrier layer disposed on a substrate surface;

- exposing the substrate to a first copper solution comprising complexed copper ions and having a pH value of less than 7;

- applying a first electrical bias across the substrate surface to chemically reduce the complexed copper ions and to deposit a copper seed layer onto the ruthenium barrier layer; and

- depositing a copper gap-fill layer by:

- exposing the substrate to a second copper solution comprising free-copper ions; and

- applying a second electrical bias across the substrate surface to deposit the copper gap-fill layer onto the copper seed layer.

60. (New) A method for depositing a copper-containing seed layer onto a barrier layer, comprising:

providing a substrate comprising the barrier layer disposed on a substrate surface, wherein the barrier layer has a barrier surface selected from the group consisting of a tungsten surface, a tungsten nitride surface, a titanium surface, a titanium nitride surface, a cobalt surface, a ruthenium surface, a nickel surface, and a silver surface;

exposing the substrate to an electroplating solution comprising complexed copper ions that have more negative deposition potential relative to free copper ions to deposit a copper seed layer directly on the barrier layer; and

thermally annealing the substrate in an environment containing hydrogen gas.